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At-line characterisation of compounds evolved during biomass pyrolysis by solid-phase microextraction SPME-GC-MS

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Abstract

At-line sampling by solid phase microextraction (SPME) followed by GC-MS analysis was investigated as a fast analytical method to identify and quantify the compounds evolved during intermediate pyrolysis of biomass. A 75 μm carboxen/polidimethylsiloxane (CAR/PDMS) coated fiber in retracted configuration was inserted at-line during pyrolysis at 500 °C with a bench scale fixed bed pyrolyser of different biomass substrates, lignocellulosic feedstock, agricultural wastes, animal residues and algal biomass. The molecular composition resulting from SPME sampling was compared to the chemical composition of collected pyrolysis liquid, which included the aqueous and organic phase (bio-oil). The storage capacity of the SPME fiber was tested 48 and 96 hours after sampling under air atmosphere and vacuum-packed plastic bags. The SPME-GC-MS profiles could be utilised to gather information on the characteristics of pyrolysis process, such as the efficiency of vapour condensation.

1. Introduction

Pyrolysis oil also known as bio-oil is a complex mixture of hundreds of polar and non-polar compounds formed during the thermal degradation of the main biomass components. Bio-oil composition varies depending on feedstock and process conditions [1-3].

Bio-oil contains approximately 20% water, 40% GC-detectable compounds, approximately 15% non-volatile HPLC-detectable compounds and 25% high molecular lignin [4-7]. Bio-oil from lignocellulosic biomass is mainly constituted by pyrolysis products originated from plant biomolecules (cellulose, hemicellulose, and lignin). Pyrolysis of lignin produces phenols and methoxyphenols (guaiacyl and syringyl moieities) while cellulose and hemicellulose give

furans, aldehydes, ketones and anhydrous sugars (i.e. levoglucosan and anhydro xylopyranose, from cellulose and hemicellulose, respectively). This mixture of polar and non-polar compounds makes the chemical characterisation extremely difficult and laborious and requires the use of several analytical techniques (i.e. GC-MS, HPLC-MS, and GPC) and chemical procedures (e.g. derivatisation [8, 9], solvent fractionation [10])

The chemical characterisation at a molecular level is often accomplished by direct GC-MS of the oil (condensed organic fraction) dissolved in an appropriate solvent after pyrolysis has occurred. However, the large variety of constituents ranging from polar hydrophilic to highly hydrophobic compounds may render the choice of the appropriate solvent difficult as certain solvents are immiscible with certain constituents of the bio-oil. Moreover, the distribution of the pyrolysis products in different liquid fractions, generally a bio-oil and an aqueous solution is an additional analytical complication. This leads to inefficiencies in the spectrum of detectable compounds during GC-MS analysis. Therefore, knowledge of hot pyrolysis vapours could be useful to obtain information on the complete composition of the liquids before their condensation in the cold traps. A solvent-less technique capable of hot gas phase analysis such as solid phase microextraction (SPME) is ideally suited for this purpose.

Solid phase microextraction is a sample preparation and sampling technique developed by Pawlizny in 1990 [11,12] which has been employed on a wide range of analytes and for several applications in various research fields, such as environmental chemistry, forensic chemistry and pharmaceutical and food industries [13-17]. It allows a fast and solvent-free sampling and it is mainly applied coupled with GC-MS or other chromatographic techniques [18].

Previous works have shown SPME can be applied downstream of pyrolysis (Py-SPME) evolved by thermal desorption and pyrolysis, which de-couples the thermal conversion process and the GC-MS analysis, thus providing information on the actual composition of native vapours with simple and solventless technique [9, 16]. Other works showed SPME application by derivatisation headspace SPME (D-HS-SPME) followed by GC-MS for determination of low molecular mass aldehydes in bio-oil [8].

Several studies investigated the application of SPME for direct sampling of gaseous streams from thermochemical conversions, showing the potential of this technique for the on-line monitoring of plant operations [19-23]. This could be quite useful in the case of a distributed biomass/waste conversion schemes based on small scale intermediate pyrolysis where continuous quality control checks are necessary to ensure consistent final product.

Then, SPME sampling turns out to be a useful method as it is fast, solventless and able to give detailed information on the chemical composition of bio-oil. In addition, SPME could be coupled with several analytical techniques. Direct SPME-GC-MS analysis can gives information on the volatiles and semi volatiles compounds. However, by proper derivatisation on headspace, SPME is also able to detect polar compounds (e.g. anhydrous sugars) [9].
Finally, being the fiber reusable, the costs can be reduced in high sample throughput [24].
The aim of this study is to evaluate the SPME sampling directly within the bench scale pyrolysis reactor in order to apply the SPME as *at-line* fast method for the characterisation of several pyrolysis products evolved during the pyrolysis process.
An in-depth literature review revealed that there are no studies using SPME-GC-MS as an analytical technique applied to a bench scale pyrolysis in order to evaluate the pyrolysis in order to obtain a comprehensive spectrum of pyrolysis vapours formed with detailed comparisons made condensate bio-oil post pyrolysis.
Furthermore, the storage capacity has been tested to evaluate its ability to accurately analyse products post experimentation.
In this study, captured products were stored for periods of 48 and 96 hours in order to determine the accuracy of analysis after extended periods of time in storage, determined on a qualitative and quantitative.

2. Experimental

2.1 Feedstock

A pelletized solid digestate deriving from an anaerobic digestion plant operated by Neue Energie Steinfurt GmbH, Germany (NESt) using a mixture of maize silage (62%), cattle slurry (17%), pig slurry (17%) and cereals (4%) was used as a feedstock [25].
Other biomass samples were from woody (pine sawdust), herbaceous (switchgrass, cornstalk) [26], microalgae (Spirulina, *Arthrospira platensis*), animal residues (poultry litter) from a local poultry farm and agricultural wastes (olive residues).

2.2 At-line SPME sampling in a bench scale reactor

The SPME fiber tested was a 75 μm Carboxen/polidimethylsiloxane (CAR/PDMS) coated fiber (Supelco) used in retracted fiber configuration. Biomass samples (approximately 6-7 g) were pyrolysed using a fixed bed tubular quartz reactor previously described [27] modified with the addition of a quartz T-junction for the SPME sampling (Figure 1).

The SPME fiber was placed through a tee-joint in quartz upstream of the cold salt-ice trap (ca. - 15°C) where the oil was condensed. The pyrolysis experiments were performed at 500°C for 5 min under nitrogen flow set a 1000 mL min^{-1}. At the end of the pyrolysis run the SPME fiber was promptly subjected to GC-MS analysis.

The pyrolysis liquid collected in the cold trap was centrifuged at 3000 rpm for 15 minutes to separate the low viscous aqueous phase (AP) from the tarry dark brown bio-oil (BO). The yields of the various fractions (char, aqueous phase and bio-oil) were determined by weight difference.

2.3 Analysis of pyrolysis liquid

The chemical composition of pyrolysis liquid was determined by solvent fractionation according to the method by Oasmaa and E. Kuoppala [28] slightly modified (ethyl acetate in place of ethyl ethers and lower sample amount).

After the separation into aqueous phase and bio-oil, 1 mL of aqueous phase was taken and added 9 mL of water. Then, the mixture was placed in the centrifuge at 3000 rpm for 10 min. The water insoluble fraction was determined by weight of the formed precipitate after centrifuge. The water soluble fraction was further extracted with 10 mL of ethyl acetate (1:1 v/v) in a separation funnel and let the solution to settle. The ethyl acetate solution was decanted from the bottom and evaporated in a rotary-evaporator at 40°C. Concentration of the water soluble-ethyl acetate insoluble fraction was determined by BRIX method [10]. The same procedure was applied to the bio-oil using 1 g diluted into 10 mL of water.

The following fractions were quantified: water solubles, WS, divided into ethyl acetate soluble, EAS, (furans, phenols etc.) and insoluble, EAI, (sugars determined by the Brix method) and water insoluble, WIS, (pyrolytic lignin, extractives). The water content was determined by Karl Fischer titration.

Bio-oil elemental analysis was performed by combustion using a Thermo Scientific Flash 2000 series analyzer.

For bio-oil, GC-MS analysis was performed on 1% solution w/v in acetone/cyclohexane 1/1 v/v spiked with 0.1 mL internal standard solution (100 mg/L 1,3,5-tri-*terz*-butylbenzene), for the aqueous phase a 10 % solution v/v in acetonitrile spiked with 0.05 mL internal standard solution (5000 mg/L butanoic acid, 2-ethyl).

2.4 *GC-MS analysis*

SPME and bio-oil analysis were performed with a 6850 Agilent HP gas chromatograph connected to a 5975 Agilent HP quadrupole mass spectrometer (EI 70 eV, at a frequency of 1.55 scan s^{-1} within the 10-450 *m/z* range). Analytes were separated by a HP-5 fused-silica capillary column (stationary phase poly [5% diphenyl/95% dimethyl] siloxane, 30 m, 0.25 mm i.d., 0.25 mm film thickness) using helium as carrier gas with the following thermal program: 50°C with a hold for 5 min, then ramping up with a heating rate of 10°C min^{-1} until 325 °C followed by a column cleaning at 325 °C for 10 min. SPME desorption was performed at 280°C in the injection port in splitless mode.

The total sum area of GC detectable compounds was quantified in terms of absolute concentration using the internal standard.

A set of 27 compounds was quantified in terms of percentage relative abundance (% peak area to the total area).

All the experiments were run in duplicate. The precision was assessed by triplicate runs of SPME and bio-oil analysis of digestate sample and assumed to be representative of all biomass feedstock.

Percentage relative standard deviations (%RSD) were calculated for each pyrolysis product.

Aqueous phase analyses were performed with a Varian 3400 gas chromatograph equipped with a polar GC column (Agilent Q7221 J&W nitroterephthalic-acid-modified polyethylene glycol DB-FFAP 222 30 m, 0.25mm, 0.2 μm) and connected to a Saturn 2000 ion trap mass spectrometer (Varian Instruments) using an incident electron energy of 70 eV, in full scan acquisition (10-650 *m/z*). The following thermal program was used: 50°C with a hold for 5 min, then ramping up with a heating rate of 10 °C min^{-1} until 250 °C followed by a column cleaning at 250 °C for 5 min.

A set of 21 compounds was quantified (% peak area to the total area).

The precision was assessed by triplicate runs of aqueous phase analysis of digestate sample.

2.5 Ageing tests

For storage investigations, ageing tests on the SPME fiber were performed after sampling the vapours from the pyrolysis of digestate. The experiments were carried out by storing the fiber, after sampling, for 48 hours or 96 hours at room temperature (20±1°C) under two different storage conditions: under air atmosphere or in vacuum. To get the vacuum the needle containing the fiber was placed (without holder) in a plastic bag and vacuum sealed with a commercial vacuum sealer system for food (Krups Vacuum sealer Type 383) and finally placed into a drawer

After the storage period, thermal desorption was applied by GC-MS.

The GC-MS analyses were performed with the apparatus used for SPME and bio-oil analysis previously described in section *2.4*. The precision was assessed by triplicate runs for each condition.

3. Results and discussion

3.1. Bulk analysis of pyrolysis liquids

Bio-oils from several biomass were obtained by means of intermediate pyrolysis at 500 °C for 5 minutes.

Elemental analysis, GC-MS and solvent fractionation procedure (Table 1) were performed on both the aqueous phase (AP) and bio-oil (BO). Under the pyrolysis conditions, phase separation was observed with all tested samples, yielding an organic product with minimal water content and a aqueous product characterized by high water content (>40 %).

Furthermore, the yields of the bio-oil showed high variations between 49 % (Spirulina) and 7 % (Bark) depending on the original feedstock. [29]

The digestate sample showed a liquid composition and liquid yield in accordance with that obtained by Neumann and coworkers [25] processing the same feedstock on a 2 kg/h laboratory scale thermo-catalytic reforming (TCR®) reactor [30].

It can be observed that the bio-oil contained high carbon percentage comprising between 50.3 % and 71.8 %. Concerning nitrogen, bio-oil from woody feedstock showed low N percentage (less than 1.5%), Olive residues and digestate had a N percentage of 0.9 % and 2.8 %, respectively. OP from poultry litter and spirulina showed highest N percentage with 11.4 and 9.4 %, respectively, according to others works [31, 32].

The aqueous phases were characterized by high water content, especially the digestate sample with 75 %.

The lower water content was found in spirulina (17%).

Results from solvent fractionation showed that the water insoluble percentage fraction (WIS) is similar to the yield to bio-oil (correlated with R = + 0.97). This suggests that separation of organic and a water phase is almost complete in the sample as produced from pyrolysis. [33].

3.2. GC-MS analysis (Bio-oil)

Table 2 shows the GC-MS qualitative and quantitative results obtained from the direct GC-MS analysis of several bio-oils from different biomass. Chromatograms of bio-oils (Figs. 2 and 3) from lignocellulosic biomass (pine sawdust, switchgrass, cornstalk and bark) showed

many similarities due to the preponderant lignocellulosic matrix and differences cause by the different lignin structure. Chromatograms were meanly featured by lignin pyrolysis products such as phenols, methoxy phenols (guaiacols) and dimethoxy phenols (syringols) and by cellulose pyrolysis products such as furaldehyde, 1-methyl cyclopente-1-one and 3-methyl cyclopentane-1, 2-dione. Switchgrass and cornstalk chromatograms are characterized by high relative abundance of phenolic moieties, with 4-vinyl phenol as the most abundant compound, in accordance to lignin composition of herbaceous biomass [34]. Instead, pine sawdust (softwood) bio-oil shows a preponderance of guaiacyl moieties with low levels of syringyl moieities. Bio-oil from bark (hardwood) is dominated by both the moieties, in accordance to lignin composition of softwood and hardwood biomasses [35, 36].

Poultry litter bio-oil is mainly characterized by fatty acids (34 % palmitic acid and 16% oleic acid) from the poultry manure and by phenolic compounds (phenol and guaiacols) from the lignocellulosic fraction of the bedding material. Nitrogen containing compounds were also detected (4.0% indole, 2.7% hexadecanamide and 2.2 % methyl indole) derived from proteinaceous material of manure.

Olive residue was mainly characterized by oleic acid (22%) and phenolics compounds with guaiacol as the most abundant peak (14%) following by 4-vinyl guaiacol (8.5%), syringol (8.3%) and *trans*-isoeugenol (8.9%)

Spirulina produced bio-oil that contained high percentage of nitrogen containing compounds according to others works [37, 38]. The most abundant compounds are indoles such as indole (25%) and methyl indole (6%) and phenols such as phenol (25%) GC-MS analysis also indicates a striking presence of alkane compounds mainly characterized by heptadecane (24%) probably derived from the decarboxylation of palmitic acids.

3.3 GC-MS analysis (Aqueous phase)

Examples of chromatograms of the aqueous phase are depicted in Figure 4, while Table 3 shows the relative distribution (% peak area). Acetic acid was clearly detected in the GC polar column and represented a relatively abundant pyrolysis product of all the aqueous-phase samples. Glyceric acid was also tentatively identified in most of the samples, probably derived from sugar fragmentation in Maillard reaction [39].

In general, the aqueous phase (AP) contained compounds that were also present in the bio-oil (BO) indicating a loss of potential substances, and then a decrease of the relative abundance in the bio-oil compared to pyrolysis vapours detected by SPME". These compounds comprised lignin phenols and sugar derivatives (furaldehydes and cyclopentenones) [40, 41].

A notable exception was the olive residue, in which the aqueous phase seemed poor in organic compounds.

3.4 SPME-GC-MS

Typical chromatograms from SPME at-line sampling of pyrolysis vapours are depicted in Figure 2 and Figure 3. Each SPME chromatogram is place side by side with the corresponding GC-MS of the bio-oil for direct visual comparison. As expected, SPME allowed the detection of highly volatile pyrolysis products that could not be revealed with the direct analysis due to the presence of solvent. Volatile pyrolysis products were tentatively identified by single ion quantitation on the basis of a previous study [15] as methanol (*m/z* 31), acetone (*m/z* 58), acetic acid (*m/z* 60), and hydroxyacetone (*m/z* 43).

Important similarities can be seen in the elution region of the semi-volatiles of the vapours and BO that were featured by the same suite of pyrolysis products. Differences and similarities were investigated on a quantitative basis by the relative distribution expressed as % peak area of selected compounds (Table 2). Nitrogen containing compounds, fatty acids and sterols were not included because of they were not revealed in most of the biomass pyrolysates.

The relative distribution of the selected compounds in vapour phase sampled by SPME and those condensed in the BO were plotted in Figure 5 collectively for all the investigated biomass samples. A satisfactory linear correlation (R= + 0.81) was found when considering all the compounds. Further correlations, grouping the pyrolysis products on the basis of chemical families, were evaluated. The pyrolysis products have been divided in phenols and cellulose derivatives compounds as the most abundant compounds. The lignin phenols and cellulose derivatives compounds (Fig. 5) showed a good correlation (with R coefficient respectively of + 0.85 and + 0.82). This finding indicated that the composition of vapours determined by SPME sampling provided a reasonably prediction of the composition of the condensable bio-oil with regard to the semi-volatile fraction. However, the similarity seems to be dependent on the biomass substrate as evident by the linear correlation coefficients resulting from each single biomass (last raw of Table 2). Good linear correlations (R > + 0.8) were found for pine wood, switchgrass, olive residues and spirulina, while less satisfactory (R < + 0.8) were calculated for cornstalk, bark, poultry litter and digestate.

In general, the observed differences could be explained by lower molecular weight compounds (LMW) more abundant in the SPME. This can be due to several factors, a higher affinity of the CAR/PDMS fiber towards LMW compounds which are more effectively sorbed onto the CAR micro-porous structure [42], incomplete trapping of LMW compounds

in the cold traps [20], and distribution of polar LMW compounds (e.g. acetic acid) into aqueous phase.

3.5 Fiber storage capacity

The capacity of the fiber to trap the sorbed pyrolysis products under appropriate conditions was investigated in the case of pyrolysis experiments with digestate. The fiber was stored for 48 and for 96 hours after the sampling before GC-MS analysis. The total peak area of selected compounds (Table 2) was reported in Figure 6. Although a decrease in GC detectable compounds was observed with ageing the effect was not significant as intense GC traces could still be obtained that enabled the identification and quantitation of the main compounds (Figure 7).The percentage of the compounds retained by the fiber is higher (66%) when the fiber is stored in the vacuum-packed bag for 48 hours, but for longer periods (96 h) or under air atmosphere the percentage is around 45%.

Thus, the analytes remained trapped in the fiber without excessive degradation and volatilisation when stored under air and vacuum-packed bags.

Results obtained are in accordance with those reported by Müller and coworkers [23], who have investigated storage capacity of several SPME fibers at different times from 5 minutes to 24 hours, and at different temperatures (24 °C, 4°C and -70°C) reporting percentages of the analytes retained by the fiber (CAR/PDMS) between 30% and 85% after 24 h of storage at room temperature. However, significant differences from coating to coating were observed.

The relative distribution (Fig.7), although rather similar, generally showed, as expected, a decrease in the relative abundance of pyrolysis products with LMW (more volatiles) such as phenol, 2-methyl phenol and 4-methyl phenol, that decrease by about 40% and 60%, respectively, after 48 and 96 h under air atmosphere and by about 53% and 46% respectively after 48 and 96 h in vacuum-packed bag. However, at 48 h and 96 h storage under air atmosphere, some compounds (above all #1, #3, #8 and #19 which are furaldehyde, 1-methyl cyclopenten-1-one, guaiacol and acetosyringone, respectively) showed relative abundance higher than those after sampling at 0h. We consider that this behavior could be caused by secondary contaminations during the storage under air atmosphere, in accordance with Müller et al., [23], who have affirmed that outer environment can produce some contaminations.

Nevertheless, the feasibility of on-site sampling with a SPME device can be confirmed. In addition, SPME could be applied for a simple online monitoring of a small distributed pyrolysis plant.

4. Conclusions

The results of this study conducted on eight different kind of biomass substrates demonstrated that at-line sampling by solid phase microextraction in a bench scale pyrolysis reactor can provide relatively accurate qualitative/semiquantitative analytical information. The chemical composition obtained from at-line sampling by SPME of the vapours evolved during pyrolysis was similar to that of the resulting pyrolysis liquid. SPME provided additional information about the compounds that could be lost by ineffective trapping of the vapours or those distributed into the aqueous phase. The similarity depended on the feedstock and in general was higher for lignocellulosic biomass.

This procedure can be proposed as potentially applicable for the online monitoring of pyrolysis reactors in the production of bio-oil or biochar, or to predict the composition of tars that may contaminate syngas in gasification plants. It was demonstrated that the fiber can be stored in tightly closed plastic bags under vacuum for 4 days before GC-MS analysis.This possibility could be of interest in those situations where the reactor and laboratory are in different places.

Moreover, SPME sampling could represent a helpful tool for bio-oil sampling/analysis that could be employed for monitoring the pyrolysis process avoiding sample collection and sample pre-treatment thus reducing laboratory working time.

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Captions to figures

Figure 1: Bench scale reactor with the addition of a quartz T-junction for the SPME sampling

Figure 2: Total Ion Chromatograms from direct GC-MS analysis of bio-oil and SPME-GC-MS of vapours from preparative pyrolysis with a bench scale reactor of pine sawdust, bark, cornstalk and switchgrass. Numbers correspond to the products in Table 2. In the curly bracket the volatiles products identified: hydroxyacetaldehyde; acetic acid; acetone; hydroxyacetone; 3-pentanone

Figure 3: Total Ion Chromatograms from direct GC-MS analysis of bio-oil and SPME-GC-MS of vapours from preparative pyrolysis with a bench scale reactor of digestate, spirulina, poultry litter and olive residues. Numbers correspond to the products in Table 2. In the curly bracket the volatiles products identified: hydroxyacetaldehyde; acetic acid; acetone; hydroxyacetone; 3-pentanone

Figure4: Total Ion Chromatograms from aqueous phase. Numbers correspond to the products in Total Ion Chromatograms from direct analysis of bio-oil and from SPME of vapours preparative pyrolysis with a bench scale reactor. Numbers correspond to the products in Table 3.

Figure 5: All-biomass linear correlation between the relative distribution (% peak area) of compounds observed by direct GC-MS analysis bio-oil and from SPME sampling of pyrolysis vapours (*A:* plotting all pyrolysis products; *B:* plotting phenolic fraction*; C:* plotting cellulose derivatives compounds)

Figure 6: Total GC-peak areas from SPME of vapours from digestate pyrolysis. GC-MS performed soon after sampling (0 h) and after 48 and 96 hours storage and under air atmosphere and in vacuum packed bag (mean values and standard deviation (n=3))

Figure 7: Products distribution from SPME-GC-MS analysis of digestate soon after sampling (0h) and after storage 48 and 96 hours in vacuum-packed bags (above) and under air atmosphere (below). Numbers in x-axis correspond to the compounds in Table 2

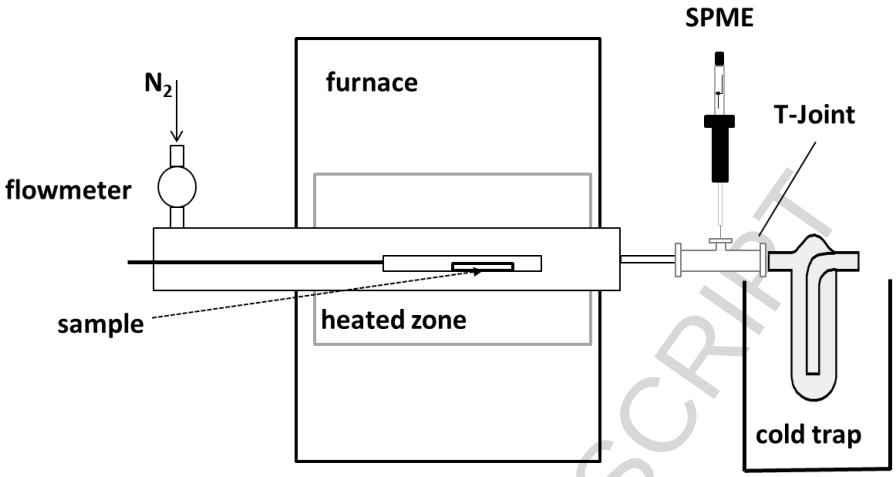

Figure 1

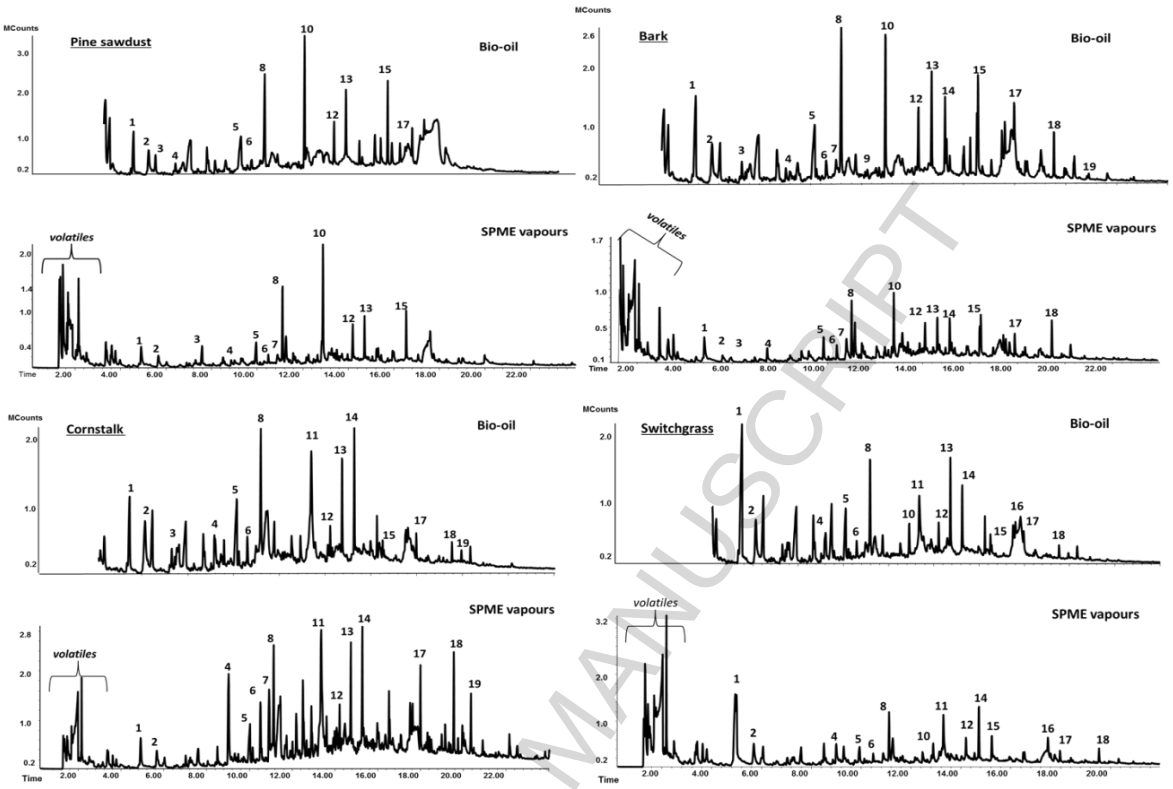

Figure 2

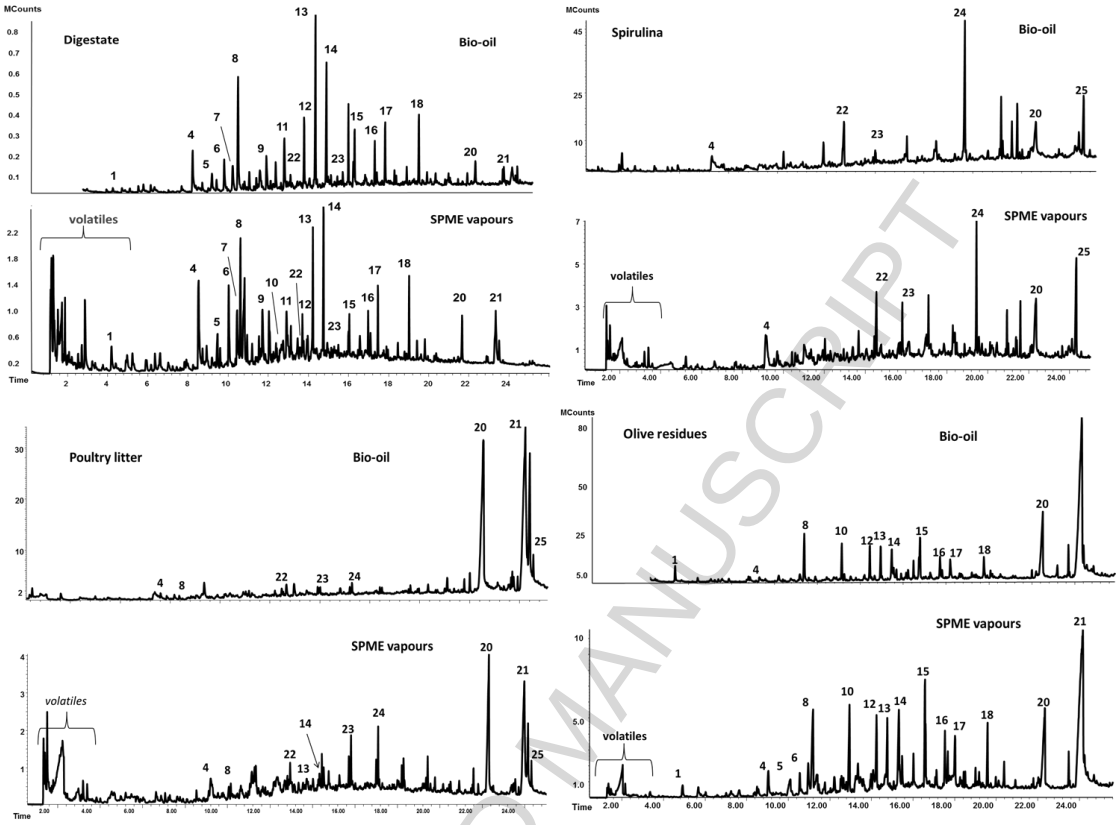

Figure 3

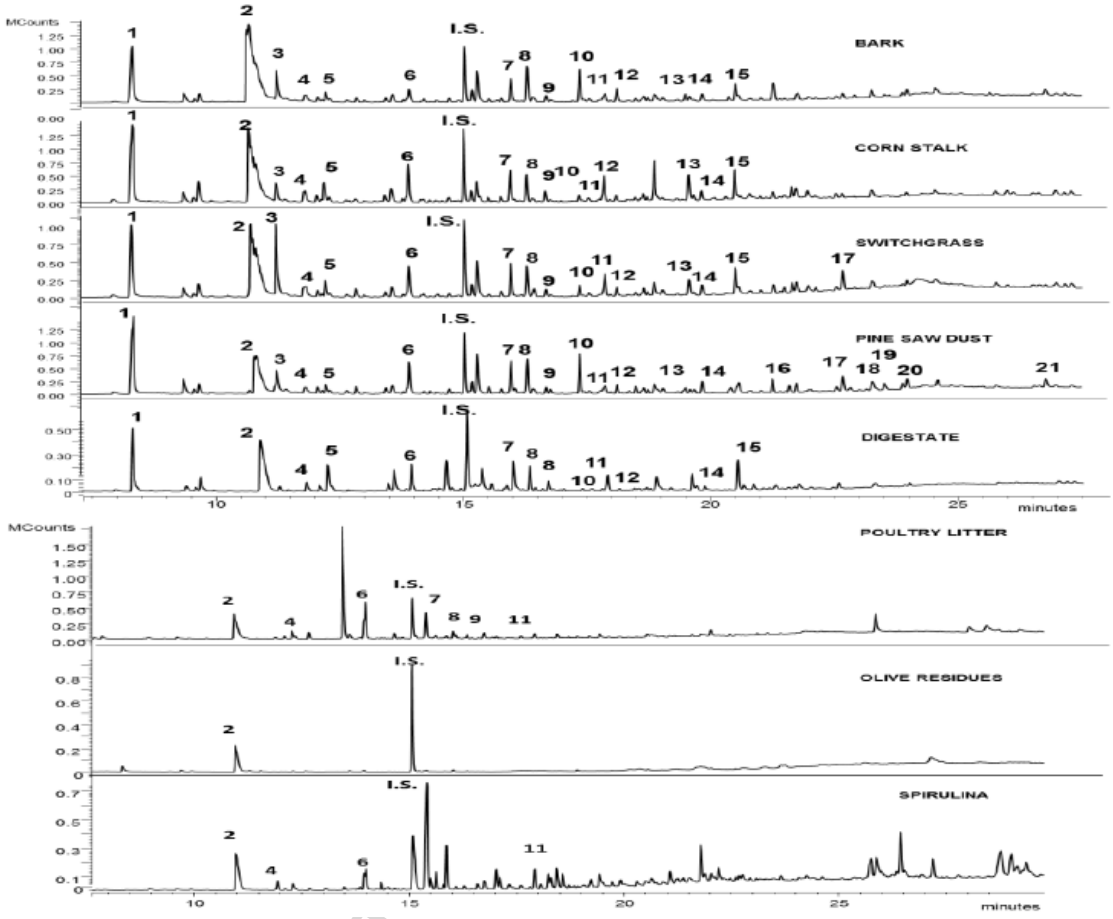

Figure 4

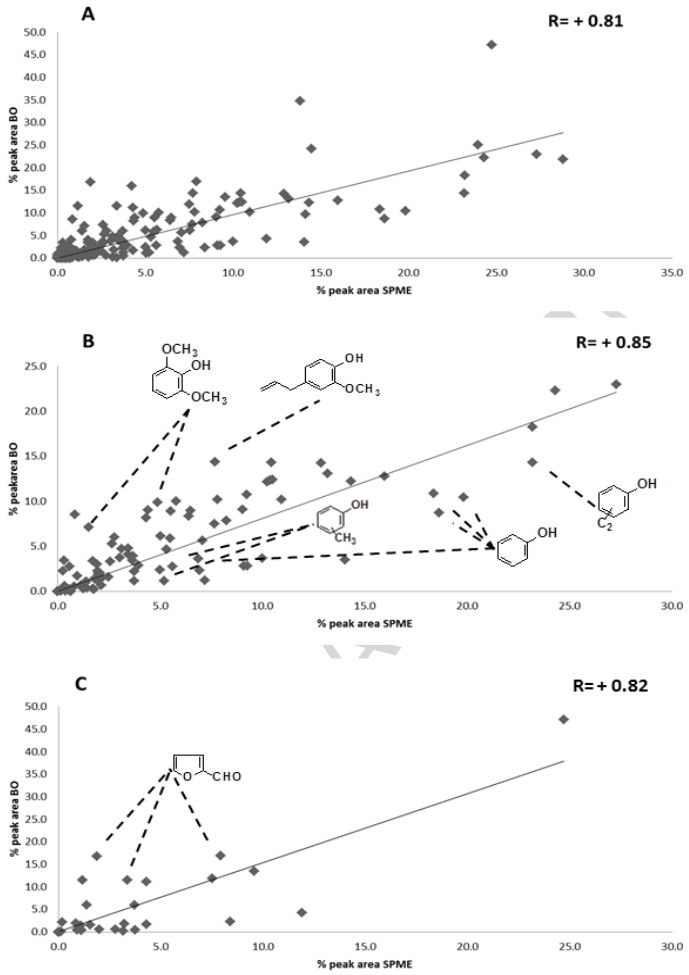

Figure 5

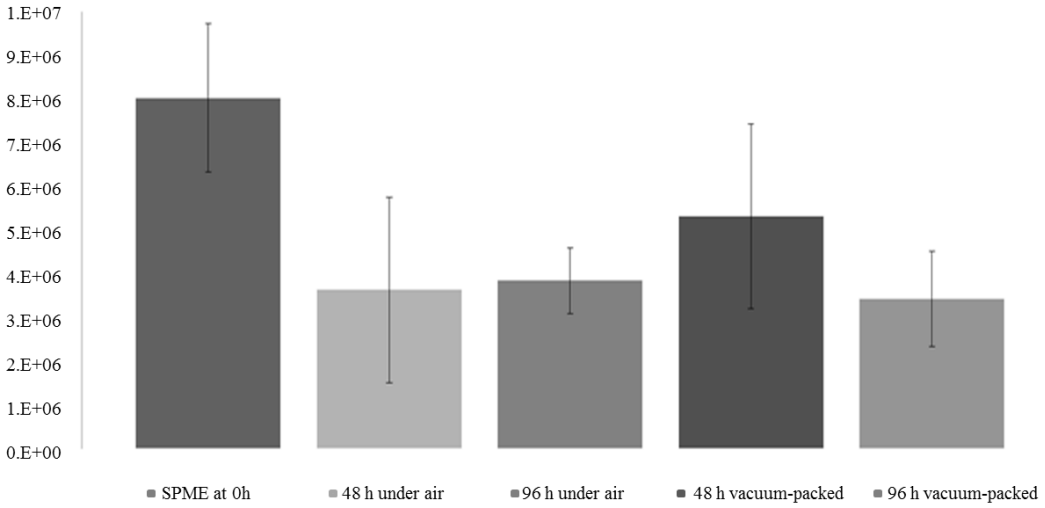

Figure 6

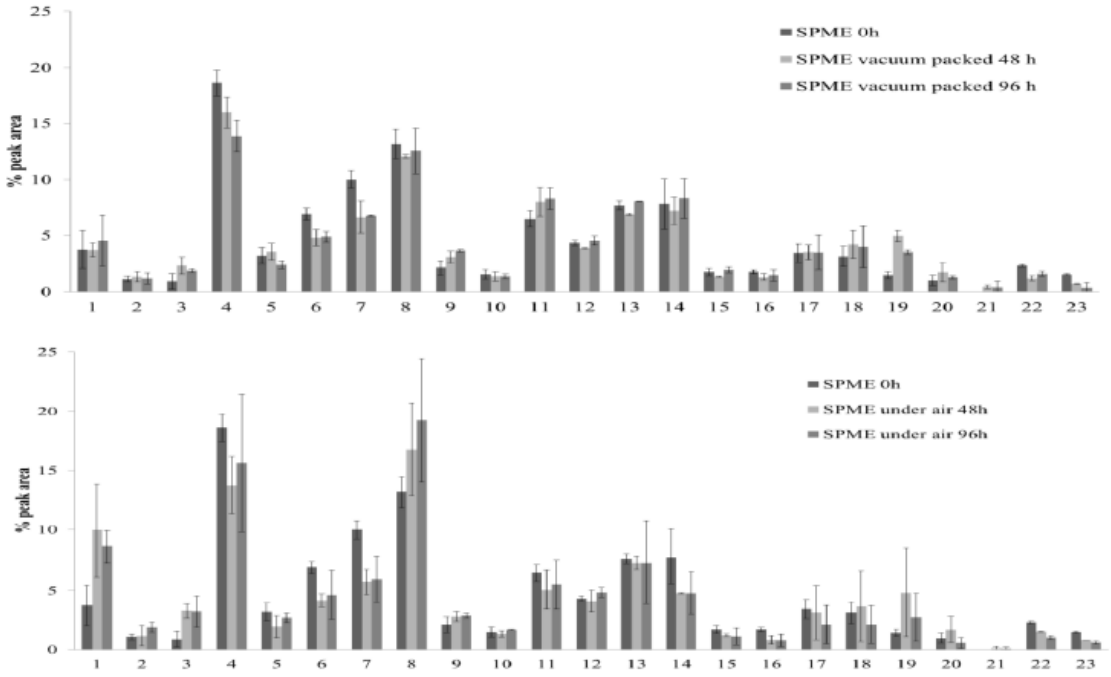

Figure 7

Table 1: Pyrolysis at 500 °C/5 min of different biomass feedstock. Yield of the total liquid and the bio-oil (BO). GC-MS (absolute concentration of total sum detectable areas). Elemental analysis, water content and composition by solvent fractionation of the liquid WS: water solubles, divided into: EAS (ethyl acetate soluble) and EAI (ethyl acetate insoluble); WIS: water insoluble

									WS		WIS
parameters → biomass ↓	Yield (wt%)	Yield BO (wt%)	GC ∑area BO (μg mg^{-1})	GC ∑area AP (μg mg^{-1})	C	H	N	Water %	EAS	EAI	
digestate	40.2	10.1	194	17	67.2	7.8	2.8	74.7	1.1	14.5	9.3
pine sawdust	42.2	18.1	83	48	55.6	6.1	0.1	32.8	6.9	32.1	14.8
cornstalk	34.7	19.2	206	41	53.8	6.1	1.5	38.5	5.4	30.0	10.5
switchgrass	33.4	9.1	143	43	51.2	6.5	1.1	50.8	4.7	26.4	1.5
bark	35.1	7.0	222	74	61.5	6.5	0.5	43.3	6.5	31.8	2.0
olive residues	38.9	28.3	161	24	71.8	2.4	0.9	35.8	4.0	17.5	22.5
poultry litter	31.0	35.9	131	n.d.	63.4	8.9	11.4	33.5	2.7	19.6	23.2
spirulina	26.7	48.5	112	24	64.1	8.3	9.4	16.6	4.1	25.6	41.8

Table 2: Relative distribution (% peak area) of compounds detected into the bio-oil (BO) after pyrolysis at 500°C and after at-line SPME during pyrolysis. In the last row the Pearson correlation coefficient for each biomass is showed.

	biomass		Pine sawdust		Cornstalk		Switchgrass		Bark		Poultry litter		Olive residues		Spirulina		Digestate	
#	**compound**	**m/z**	**BO**	**SPME**	**BO**	**SPME**	**BO**	**SPME**	**BO**	**SPME**	**BO**	**SPME**	**BO**	**SPME**	**BO**	**SPME**	**BO**	**SPME**
1	Furaldehyde	96	13.5	9.5	11.5	1.1	47.2	24.7	16.9	1.8	–	–	4.3	11.9	–	–	0.40	3.74
2	Hydroxypentenone	98	0.6	2.8	6.0	1.4	6.0	3.7	0.2	3.1	0.6	2.0	0.1	0.1	–	–	0.33	1.10
3	1-methyl cyclopenten-1-one	96	1.4	1.1	1.9	0.8	2.2	0.2	1.5	1.5	–	–	0.5	1.1	–	–	0.50	0.90
4	Phenol	94	2.4	5.0	10.8	18.4	12.3	10.4	3.6	6.9	10.4	19.8	3.3	2.6	23.0	27.3	8.72	18.62
5	3-methyl ciclopentane-1,2 dione	112	16.9	7.9	11.1	4.3	11.6	3.3	11.9	7.5	1.7	4.3	2.3	8.4	–	–	1.85	3.20
6	2-methyl phenol	108	1.2	3.7	2.8	9.1	3.4	3.6	2.7	5.6	4.6	5.3	1.2	1.9	5.6	7.1	2.30	6.93
7	4-methyl phenol	107	2.2	3.7	2.8	9.3	3.4	0.3	2.7	0.6	–	–	3.0	1.9	–	–	3.65	9.99
8	Guaiacol	109	22.3	24.3	10.0	5.8	14.3	10.4	18.2	23.2	5.9	5.5	14.2	12.9	–	–	13.09	13.16
9	4-ethyl phenol	122	0.2	0.5	0.2	1.8	0.2	0.4	0.2	0.4	3.5	14.0	0.0	0.2	–	–	0.66	2.12
10	4-methyl guaiacol	138	1.4	1.8	0.0	0.4	0.1	0.1	0.8	1.3	0.9	1.3	0.2	0.6	–	–	7.10	1.51
11	4-vinyl phenol	120	0.3	1.7	14.3	23.2	12.7	15.9	0.4	1.4	–	–	2.3	0.3	–	–	8.94	6.48
12	4-ethyl guaiacol	137	12.2	14.3	4.1	3.4	6.1	5.0	10.2	10.9	–	–	1.2	7.2	–	–	8.16	4.33
13	4-vinyl guaiacol	150	12.2	10.2	7.5	7.6	10.7	9.2	9.1	9.0	2.8	3.9	8.3	6.4	–	–	14.36	7.68
14	Syringol	154	0.3	1.2	9.9	4.9	9.0	4.4	1.2	5.2	2.3	1.9	8.5	0.8	–	–	10.20	7.80
15	Trans-isoeugenol	164	12.4	10.5	0.5	0.8	1.1	1.4	7.8	8.2	1.7	1.0	8.9	5.5	–	–	3.38	1.72
16	Syringaldehyde	182	0.0	0.5	1.3	1.0	1.8	1.5	3.6	2.6	–	–	7.3	2.6	–	–	3.97	1.72
17	4-vinyl syringol	180	0.6	0.3	2.0	2.0	2.0	2.1	3.7	3.0	–	–	5.3	2.6	–	–	4.80	3.44
18	Methoxyeugenol	194	0.0	0.6	1.4	2.2	1.6	2.5	3.9	3.7	0.7	1.1	6.0	2.8	–	–	4.73	3.12
19	Acetosyringone	181	0.0	0.3	1.5	1.1	1.1	0.5	1.2	0.6	–	–	0.1	0.9	–	–	1.15	1.45
20	Palmitic acid	256	0.0	0.4	0.2	1.2	0.2	0.4	0.1	3.4	34.8	13.8	1.1	0.0	6.2	7.5	0.85	0.98
21	Oleic acid	264	–	–	–	0.2	–	–	–	–	16.0	4.2	21.9	28.8	–	–	0.18	0.00
22	Indole	117	–	–	–	–	–	–	–	–	4.0	0.8	–	–	25.1	24.0	1.40	2.30
23	Methyl indole	131	–	–	–	–	–	–	–	–	2.2	0.8	–	–	6.3	5.7	1.00	1.50
24	Heptadecane	57	–	–	–	–	–	–	–	–	1.0	5.0	–	–	24.2	14.4	–	–
25	Hexadecanamide	72	–	–	–	–	–	–	–	–	2.7	2.4	–	–	9.6	14.1	–	–
26	Cholesterol	386	–	–	–	–	–	–	–	–	3.4	2.0	–	–	–	–	–	–
27	Sitosterol	414	–	–	–	0.3	–	–	–	–	1.0	1.9	–	0.7	–	–	0.72	–
	Pearson correlation coeff		R=+0.92		R= + 0.63		R= +0.92		R= + 0.70		R= +0.56		R= + 0.81		R= +0.86		R= + 0.66	

Table 3: Relative distribution (% peak area) of compounds detected into the aqueous phase (AP) after pyrolysis at 500°C

#	compound	Pine sawdust	Cornstalk	Switchgrass	Bark	Poultry litter	Olive residues	Spirulina	Digestate
1	d-(+)-Glyceric acid	20.7	26.1	16.7	10.3	-	-	-	13.6
2	Acetic acid	24.7	23.4	19.9	45.0	42.5	-	67.4	31.7
3	Furaldehyde	5.6	5.1	15.0	3.9	-	-	-	1.2
4	3-methyl cyclopenten-1-one	1.2	1.5	1.1	0.8	2.4	-	1.9	1.9
5	5-methyl furaldehyde	1.4	0.7	1.8	0.7	-	-	-	0.0
6	Furfuryl alcohol	6.5	8.5	6.4	2.9	38.0	-	-	7.8
7	3-methyl cyclopenten-1,2-dione	5.6	6.1	5.8	3.7	5.4	-	-	9.9
8	Guaiacol	6.0	5.4	5.4	5.0	2.3	-	-	7.5
9	3-ethyl-2-cyclopenten-1-one	1.1	2.1	1.3	0.8	5.1	-	-	3.3
10	4 -methyl guaiacol	6.3	0.9	1.7	5.2	-	-	-	0.6
11	Phenol	1.5	5.1	4.2	1.7	4.3	-	20.0	5.4
12	4-ethyl guaiacol	1.6	1.2	1.8	1.8	-	-	-	0.6
13	2-ethyl phenol	1.3	0.9	1.1	1.0	-	-	-	0.3
14	Vinyl guaiacol	2.5	1.9	2.3	1.0	-	-	-	0.9
15	Syringol	2.4	5.2	5.1	3.6	-	-	-	10.6
16	Trans-Isoeugenol	3.4	1.7	1.9	3.5	-	-	-	1.6
17	5-hydroxymethyl furfural	2.2	1.1	4.0	1.2	-	-	-	-
18	Vanilin	1.7	2.3	2.5	2.0	-	-	-	2.0
19	Propyl guaiacol	2.1	-	0.5	1.4	-	-	-	-
20	Coniferyl alcohol	2.4	0.9	1.1	2.0	-	-	-	1.3
21	4-(ethoxymethyl)-2-guaiacol	-	-	0.6	2.7	-	-	-	-

Highlights

- At-line sampling by solid phase microextraction in a bench scale pyrolysis reactor
- SPME vapours evolved during pyrolysis was similar to the resulting pyrolysis liquid
- Application for the monitoring of pyrolysis reactors in the production of bio-oil
- Fiber can be stored in tightly closed plastic bags for 4 days before GC-MS analysis